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# Catalytic Effect Of Kieselguhr In Chlorination.

# CATALYTIC EFFECT
OF
# KIESELGUHR IN CHLORINATION

BY

JOHN BREEDIS

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## THESIS

FOR THE

## DEGREE OF BACHELOR OF SCIENCE

IN

## CHEMISTRY

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COLLEGE OF LIBERAL ARTS AND SCIENCES

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

JOHN BREEDIS

ENTITLED CATALYTIC EFFECT OF KIESELGUHR IN CHLORINATION

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY

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# CATALYTIC EFFECT OF KEISELGUHR IN CHLORINATION.

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## INTRODUCTORY.

The problem of catalysis is perhaps as old as the human race. The first catalytic reactions to attract attention were those included under the most wonderful of all the chemical processes - fermentation. Pliny gives a very good description of the fermentation of both wine and vinegar, but in the days of yore men were not really able to differentiate chemical changes of any kind, much less to measure the velocity of reaction, until the close of the eighteenth century when the new chemistry had its birth.

In 1835 Berzelius described a number of reactions of peculiar nature which he defined as catalytic. In his "Traite de Chimie" he thus defined the catalytic phenomena: "It is evident that the catalytic force acts principally on the polarity of the atoms, which is increased, diminished, or changed by it. In other words, the catalytic force is manifested by the exciting of electric affinities which up to the present have escaped our investigations."

This was a case of being satisfied with words: the language of the illustrious Swedish chemist sheds no light and is only an avowel of impotency. Neither did Mendeleeff with his supposition that "some change takes place in the motions of the atoms within the molecules at the points of contact of the latter" helped the matter much.

Since that time, however, hundreds of investigators have been

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busy working in this branch of chemistry and during recent years numerous new catalytic agents have been discovered, and certain of the older reactions studied in some detail. Prof. Ostwald and his students are among these workers. In a report found in the Zeits. fur Electrochem. 1901, 7 , 995, he classified catalytic reactions into the following four groups:

1. Separation in supersaturated solutions
2. Catalysis in homogeneous mixtures
3. Catalysis in heterogeneous mixtures
4. Action of enzymes.

His definition of "Catalysis" or "Catalytic agent", concise and, perhaps, on account of this not entirely free from objections, reads:

> "A catalytic agent is such material which affects the velocity of a chemical reaction without itself appearing in the final products."

This definition implies that reaction in any system must be not only possible, but actually taking place before a catalytic agent can produce effect. In other words, a catalytic substance is, according to Ostwald, incapable of starting a reaction; it can only affect the rate of change. It is, however, a popular misconception, for if we admit, and I think we are bound to do so, that the trace of water, shown by Dixson's classical research (1) to be necessary before explosion can take place in such gaseous mixtures as carbonic oxide and oxygen, acts catalitically, then Ostwald's definition is insufficient. This fact is illustrated by another well known example,- HCl and $NH_3$ when brought together in a perfectly dry

condition will not react with each other. The presence of the merest trace of water vapor, however, suffices to start the reaction. The mechanism of this action is not as yet understood but it seems to resemble in some respects the effect of a percussion cap in setting off an explosive. Once started the reaction is able to proceed of itself without further assistance. It seems to me that an adequate definition is impossible so long as the mechanism and the nature of the phenomenon remains unexplained. We have to be satisfied then with a simple statement "That by the aid of certain materials we are enabled to, more or less, readily effect reactions which otherwise would be either impossible or impracticable."

The number and variety of reactions susceptible to catalytic influence are almost infinite. To quote Ostwald once more: "There appears to be no kind of chemical reaction which cannot be influenced catalytically, and no form of chemical substance, be it element or compound, which cannot act as a catalyst."

The catalytic agent may be a gas or vapor, a liquid or a solid. Examples of these varieties are the water (or similar) vapor necessary for certain gaseous explosions, the nitrogen oxides in the lead chamber process, acids in sugar inversion, platinum in oxidations, nickel in reductions, etc. For some classes of work the one agent is especially applicable and useful; for other work a different agent is preferable or necessary.

The reactions affected may be those of simple combination or dissociation; reduction or oxidation, which may be partial, complete or fractional; hydrolysis, substitution, etc., together with combinations of these, ranging over both organic and inorganic chemistry. There are also cases in which the presence of a catalyst

alters in a very striking manner the course of electrolysis. The subject of photo-chemistry is being extensively investigated at the present time. Many reactions which proceed very slowly or inappreciably in the dark are greatly accelerated when illuminated by radiant energy of the proper wave length. Not only is the reaction rate influenced by the light, but the nature of the reaction products and the yield obtained are also affected. These effects although mentioned here are not usually classed as catalytic.

To simplify matters the various catalytic reactions have been divided into two general classes: (1) Those in which the catalyst actually reacts chemically with one of the reacting substances to form an intermediate compound, which in turn reacts in such a way as to regenerate the catalyst and to produce the final reaction products, and (2) those reactions which are brought about by the catalytic agent through simple contact, as indicated by Mitscherlich.[2]

The first kind of catalysis is well illustrated by iodine or the monochlor iodide which placed with organic substance in presence of chlorine gas changes itself into the trichloride, which then gives up its chlorine to the compound, returning to the state of monochloride. The chlorinated products are always mixed with some iodine derivative formed by inclusion. Of close relation to this is what M.P. Sabatier[3] calls a reciprocal catalysis, illustrated by the simultaneous destruction of hydrogen peroxide $H_2O_2$ and chromic acid $H_2CrO_4$. The decomposition of either, when left alone, is very slow, but mix the two and they will catalyse each other reciprocally in such a manner that the quantity of

oxygen liberated by the hydrogen peroxide is exactly the same as that coming from the chromic acid. This proportionality indicates the cause of the decomposition, which is the product of an unstable compound of the hydrogen peroxide and the chromic acid associated in the proportion $3H_2O_2 : 2H_2CrO_4$. As soon as formed this compound breaks up with the liberation of oxygen, leaving water and chromium sesquioxide which dissolves in the sulphuric acid used to acidulate the chromic acid and render it more stable.

The transient compound the formation of which brings about the simultaneous destruction of the two systems is no longer a myth for it has been isolated from working with dilute solutions of hydrogen peroxide and chromic acid, acidulated with sulphuric acid. Such a mixture of the two furnishes, instead of a violent evolution of oxygen, a liquid of an intense blue. Agitation with ether dissolves out the blue substance, which is precisely the temporary unstable compound. It may be isolated by evaporating the ether at $-20^{\circ}$, but decomposes into oxygen, sesquioxide of chromium and water if brought up to the ordinary temperature.

Many reactions both in the gaseous state and in solution are greatly accelerated near the surface of certain solids such as platinum black, ferric and other metallic oxides, palladium and charcoal. Such substances in a finely divided state adsorb, that is, concentrate upon their surface the reacting substances from the gas or solution and the reaction in the adsorbed layer then proceeds much more rapidly than in the body of the gas or solution where the concentrations are much lower.

The porous state of the catalyst with its gas absorbing properties seems to be the fundamental cause of catalysis with this

kind of catalytic agents. For this reason charcoal has been the object of a multitude of researches.(4) 1.57 gr. of charcoal of the cocoa nut, corresponding to one cubic centimeter of compact carbon, absorbs at 15° and 760 mm. widely varying volumes of gases, from 2 cc of argon to 178 cc of $NH_3$.

The volume given for ammonia shows that the gas, supposing it is confined within the entire volume of the charcoal, is subjected to a pressure of 178 atmospheres. The heat of absorption is greater than that of liquifaction and is nearly equal to the heat of solution of ammonia in water. These are the facts, the interpretations vary. But whatever the explanation adopted for these properties of charcoal, the absorption of the gas in its pores is equivalent to a compression of that gas to a pressure more or less high, and in the result we find that hydrogen and chlorine unite in the cold on meeting thus in the pores of the charcoal. The same is true of CO and $Cl_2$, $H_2S$ and $O_2$ and others.

## EXPERIMENTAL PART.

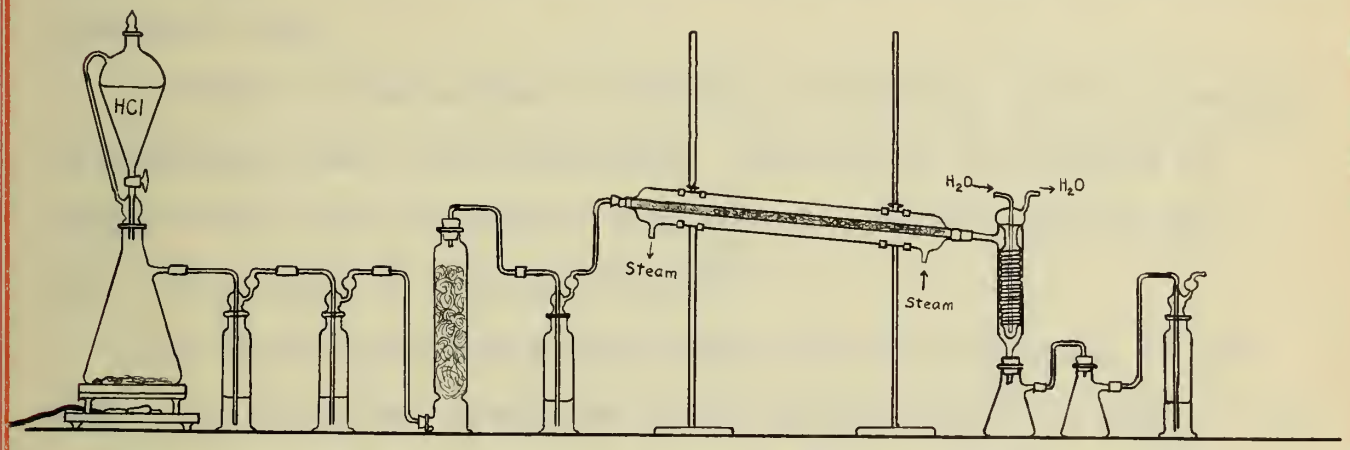
The object of the following experimental work was to find whether we can extend the analogy from charcoal to Kieselguhr as catalytic agent in chlorination on account of its physical properties. The speed of any chemical reaction is directly proportional to the product of the concentration of the reacting substances. If adsorption of chlorine by Kieselguhr takes place, the concentration of the $Cl_2$ in the Kieselguhr should be many times that of the gaseous chlorine, and hence it should react much more easily and rapidly with the other substances.

First of all the Kieselguhr itself was examined. Physically it is a very porous material composed of the skeletons of infusoria. The sample worked with had a pink tinge probably due to the presence of iron. A qualitative analysis was made, with results corresponding approximately to those found in the American Chemical Journal. 19: 235,(1897)

| $SiO_2$ Amorphous | $SiO_2$ Crystal | $TiO_2$ | $Fe_2O_3$ | $Al_2O_3$ | MgO | CaO | $H_2O$ at 100° | Water and Organic matter by ignition |
|---|---|---|---|---|---|---|---|---|
| 65.83% | 14.65% | 0.4% | 2.34% | 4.17% | .71% | trace | 4.13% | 7.50% |

The first chlorination experiments were performed on carbon bisulphide in two different ways:

I. The apparatus was arranged as in the following diagram




It was expected that the chlorine would volatilize the $CS_2$ and then together with it enter the large condenser filled with Kieselguhr. This was kept at 100° by passing steam instead of water through the outer jacket. It did not volatilize the $CS_2$ readily and the product condensed proved to be mostly $CSCl_2$, $S_2Cl_2$ and doubtless a mixture of other sulpho-chlorine combinations. It contained but a

very small amount of $CCl_4$.

Kolbe, in 1843,[5] described an experiment in which chlorine was bubbled through $CS_2$. The vapors were heated in a porcelain tube filled with broken porcelain, then condensed. Carbon tetrachloride was formed, mixed with $S_2Cl_2$. The yield, however, was not stated and therefore comparison of the two methods is impossible.

II. A modification of the above method was next tried. In this experiment the $CS_2$ was volatilized by heat and its vapors were passed into the tube where they mixed with the $Cl_2$ in the presence of the Kieselguhr. As before, the temperature was kept at 100°. The relative proportions of the products were not improved and the experiments of chlorination of carbon bisulphide were abandoned.

A study of the action of chlorine on toluene in the presence of Kieselguhr was next undertaken. The action of chlorine on toluene both with and without the use of catalytic agents has been the subject of repeated study.[6]

The first experiments were done with moist chlorine in the cold. The chlorine, generated by the action of HCl on $KMnO_4$, was washed with water and partially dried by bubbling it through a bottle of $H_2SO_4$. After three hours the toluene began to turn dark and at the end of the chlorination the product was entirely black and had a musty smell. It filtered giving a solution of the same color, probably due to colloidal carbon. When distilled the largest portion came over between 80°-90°, the temperature then went up rapidly and the product completely decomposed at 160°. Repeated experiments gave the same results.

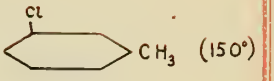
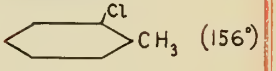
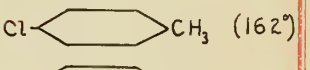
Since the moistness of the chlorine was supposed to be the

reason for the above decomposition to colloidal carbon means were taken to dry the chlorine completely. This was very effectively accomplished by introducing a drying tower filled with glass beads which were kept moistened with concentrated sulphuric acid, thus making application of the principle of counter currents. After this change was made in the drying part of the apparatus, the black solution of toluene was never obtained again.

When toluene is chlorinated in the cold without the use of a catalyst, the chlorine is substituted in the ring, while if the chlorination is carried out at the boiling point of toluene, the chlorine enters the side chain. In presence of a catalytic agent like iodine, it goes in the ring even at the boiling temperature of toluene.(7)

From the chlorination of toluene alone, and with 5% of Kieselguhr it was evident that the reaction was more vigorous in the presence of Kieselguhr than without it. With the Kieselguhr the toluene became boiling hot and begin to distil over, whereas without it, under approximately the same conditions, it did not react nearly as vigorously. The question to answer next was whether the substitution took place in the ring when hot or whether the substitution took place in the side chain under these conditions, as it should without a catalyst.

Distillation of the products of the chlorination showed that a mixture of the two was obtained. Furthermore, the substitution of the $Cl_2$ in the ring apparently had taken place in all three positions,- ortho, meta, and para, as fractions were obtained corresponding to all those boiling points, as shown by the following table:

| | | | | | | |
|---|---|---|---|---|---|---|
| Fraction I | from | 115° | to 130° | - 8.5 g. | | |
| II | " | 130° | - 140° | - 8.0 " | | |
| III | " | 140° | - 150° | - 31.5 " | corresp. to |  (150°) |
| IV | " | 150° | - 160° | - 14.0 " | " " |  (156°) |
| V | " | 160° | - 170° | - 24.0 " | " " |  (162°) |
| VI | " | 170° | - 180° | - 16.0 " | " " | (179°) |
| VII | " | 180° | - 200° | - 8.0 " | " " | ring di-and tri-substit. prod. |
| VIII | " | 200° | - 220° | - 2.5 " | " " | side chain di- and tri- substit. prod. |

It became evident that the merits of Kieselguhr as a catalyst in chlorimation should be decided by means of quantitative data.

Since the chlorine could not be measured by passing it directly into the substance to be chlorinated, it was necessary to select some medium which would hold the chlorine in solution and give it up as the reaction proceeded. Carbon tetrachloride was decided upon and since data as to solubility of chlorine in it could not be found in the literature, the carbon tetrachloride was saturated with chlorine at room temperature (23°) and analyzed. A sample of it was run into potassium iodide solution and the iodine liberated was titrated with .1 N sodium thiosulphate solution. The solubility of chlorine in carbon tetrachloride was thus found to be 8.4%.

The influence of Kieselguhr on the velocity of chlorination was studied first with benzene. The velocity of the reaction between chlorine and benzene without catalytic agents is exceedingly small and it cannot be accurately measured with ordinary apparatus. (8)

To avoid the di- and higher chlorine substitutions excess of

benzene was used. The reactions were carried out at 25°.

Exp. I. Chlorine: Benzene = 1 : 5

1 g. Kieselguhr to 7.5 g. of chlorine in a total of 150 g. of solution.

| | | |
|---|---|---|
| At the start | 5.00 | % chlorine |
| 5 min. after | 4.61 | " |
| 15 " " | (spoiled) | |
| 30 " " | 3.35 | " |
| 1 hour | 3.06 | " |
| 4 hours | 2.91 | " |
| 24 hours | 2.90 | " |

Exp. II. Chlorine: benzene = 1 : 5

2 g. Kieselguhr to 8.2 g. of Chlorine in a total of 207 g. of solution.

| | | |
|---|---|---|
| At the start | 3.96% | Chlorine |
| 5 min. after | 3.32% | " |
| 1 hour after | 2.68 | " |
| 3 hours " | 2.31 | " |
| 7 " " | 2.29 | " |
| 17 " " | 2.26 | " |

Exp. III. Chlorine : benzene = 1 : 5

5 g. Kieselguhr to 6.15 g. of chlorine in a total of 132 g. of solution.

| | | |
|---|---|---|
| At the start | 4.65% | Chlorine |
| 5 min. after | 3.65 | " |
| 1 hour " | 3.41 | " |
| 4 hours " | 3.13 | " |

The above data are shown graphically in the accompanying curves (Plate I) The slope of the curves, $\frac{dx}{dt}$, represents the amount of chlorine transformed per unit of time and is therefore a measure of the velocity of the reaction. Comparing curves I, II and III it is seen that the value of $\frac{dx}{dt}$ during the initial period is greater in the case of curve II than in the case of curve I, and the greatest of all in the case of curve III. In the case of benzene and chlorine alone $\frac{dx}{dt}$ is negligibly small. The speed of the reaction is therefore seen to be approximately proportional to the concentration of the Kieselguhr.

Exp. IV. Chlorine: benzene = 1 : 10

2 g. Kieselguhr to 5.55 g. chlorine in a total of 168 g. of solution.

| | | |
|---|---|---|
| At the start | 3.3% | Chlorine |
| 5 min. after | 2.35 | " |
| 15 " " | 2.25 | " |
| 1 hour " | 2.20 | " |
| 3 hours " | 2.18 | " |

Exp. V. Chlorine : benzene = 1 : 10

5 g. Kieselguhr to 7.3 g. of chlorine in a total of 196 g. of solution

| | | |
|---|---|---|
| At the start | 3.72% | Chlorine |
| 5 min. after | 2.96 | " |
| 20 " " | 2.56 | " |
| 45 " " " | 2.50 | " |

The above data are shown graphically on Plate II. The failure of curve II to show a greater slope than curve I in the

initial period indicates that the increased dilution brings other factors into play which destroy the approximate proportionality of speed of reaction to concentration of Kieselguhr.

Exp. VI. Chlorine : toluene = 1: 5

Without Kieselguhr, 5.1 g. of chlorine in a total of 116 g. of solution.

| | | |
|---|---|---|
| At the start | 4.38% | of Chlorine |
| 5 min. after | .63 | " |
| 10 " " | .47 | " |
| 20 " " | .45 | " |
| 45 " " | .45 | " |
| 2 hours " | .45 | " |

Exp. VII. Chlorine : toluene = 1 : 5

1 g. Kieselguhr to 5.45 g. of chlorine in a total of 117 g. of solution

| | | |
|---|---|---|
| At the start | 4.65% | of Chlorine |
| 5 min. after | 1.60 | " |
| 10 " " | 1.17 | " |
| 20 " " | 0.99 | " |
| 45 " " | 0.81 | " |
| 3 hours " | 0.45 | " |
| 15 " " | 0.0 | " |

The curves for the above data are shown in plate III. From these it is seen that the behavior of Kieselguhr in the chlorination of toluene is directly contrary to its action in the chlorination of benzene. With toluene it functions negatively instead of positively. This may be due to its action in increasing the amount

of side chain substitution (see table page 10 ), a reaction which probably goes more slowly than the nucleus substitution. It may be that Sabatier's[9] explanation of the failure of porous charcoal to catalyze effectively most gaseous reactions is true in this case. The rate at which the adsorbed $Cl_2$ is given up to the toluene may be so slow that the Kieselguhr retards rather than accelerates the chlorination. Lack of time and material did not permit further investigation of this phase of the work.

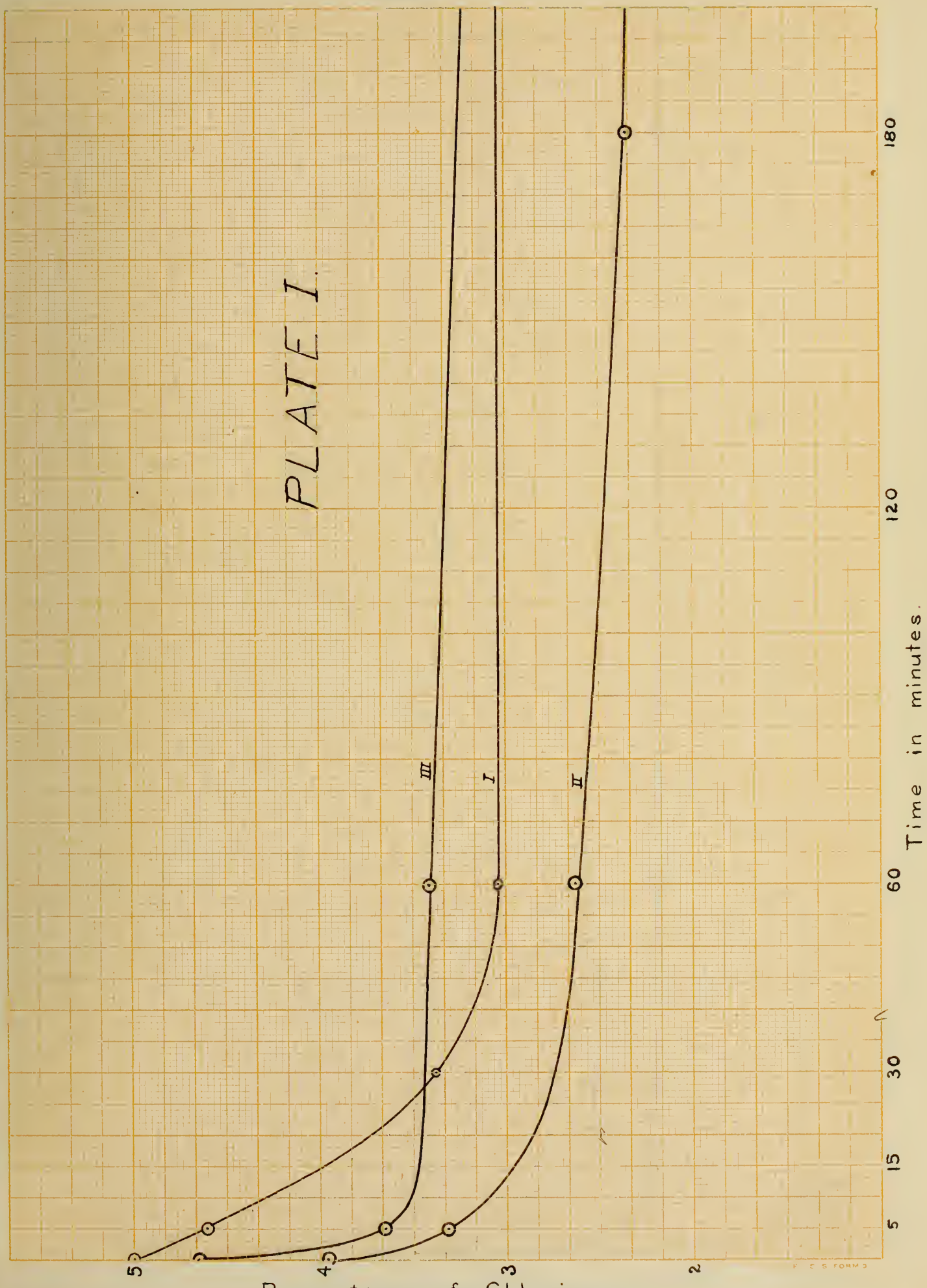


PLATE I.
III
I
II
5
4
3
2
Percentage of Chlorine.
5
15
30
60
120
180
Time in minutes.

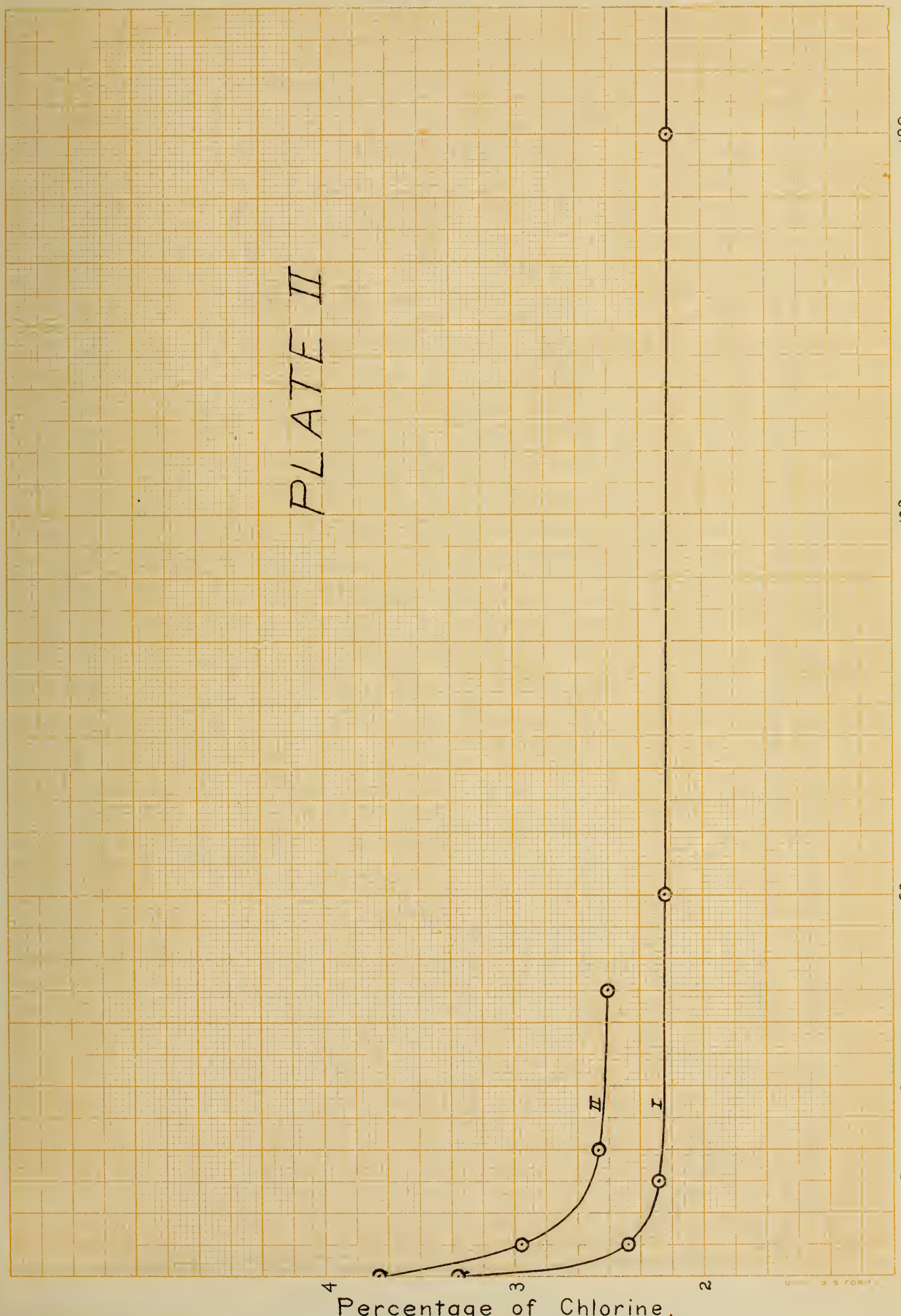


PLATE II
180
120
60
30
15
5
Time in minutes.
4
3
2
Percentage of Chlorine.
II
I

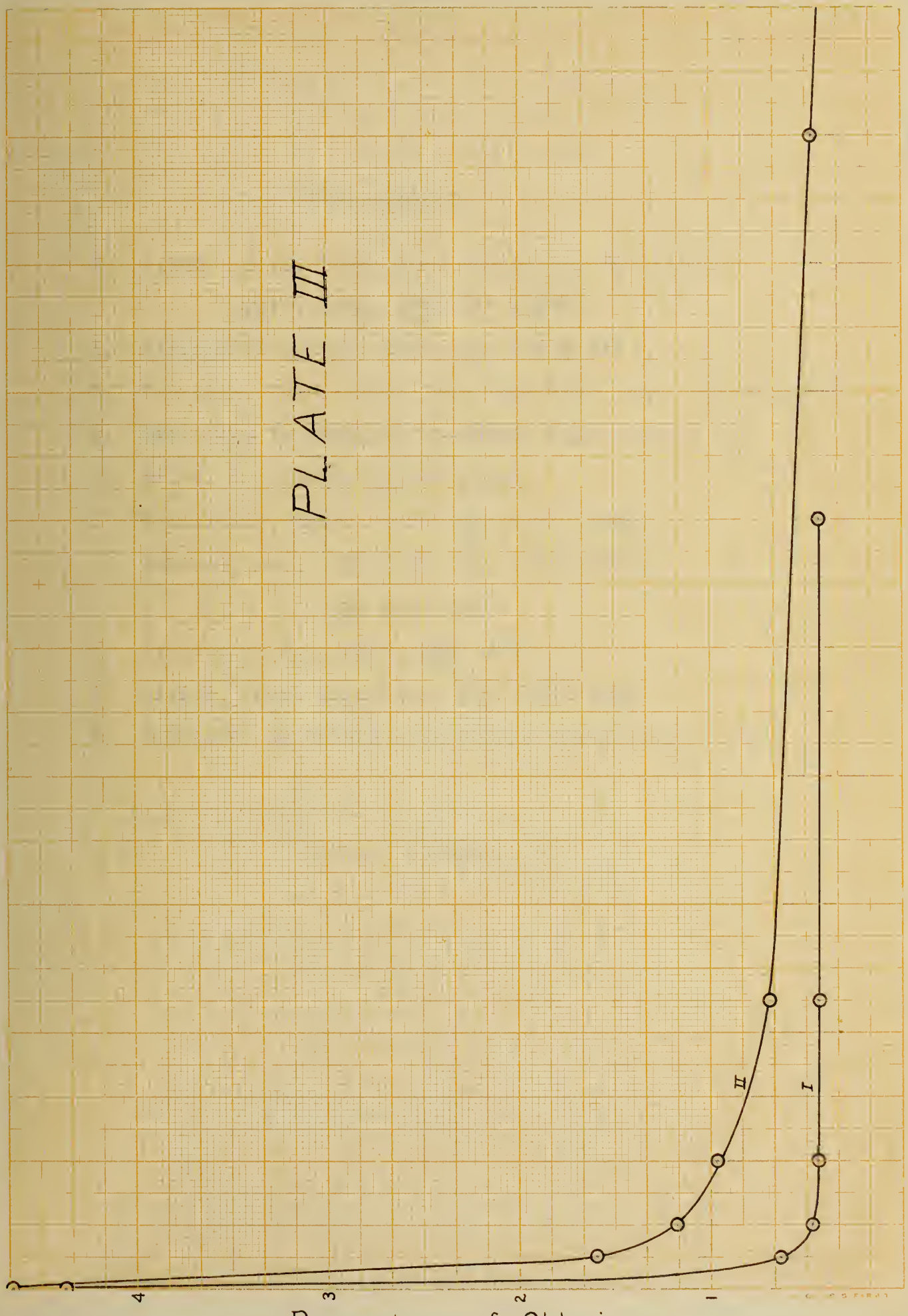


PLATE III
Time in minutes.
10
20
60
120
180
I
II
1
2
3
4
Percentage of Chlorine.

## BIBLIOGRAPHY.

1. DIxon, Jour. Chem. Soc. London 49: 94 (1886)
Phil. Tran. 175: 617 (1884)
2. Mitscherlich, Ann. Chem. 44: 186 (1842
3. Sabatier, Chem. Trade Jour. and Chem. Eng. 55: 23 (1914)
4. Sabatier, La Catalyse en Chimie Organique p. 247
5. Kolbe, Ann. Chem. 45: 41 (1843
6. Cannizzaro, Compt. rend. 41: 517 (1855)
Schramm, Ber., 18: 350, 606, 1272 (1885)
19: 212 (1886)
7. Beilstein, Ann. Chem. 139: 331
8. Slator, Jour. Chem. Soc. 83: 730 (1903)
9. Sabatier, La Catalyse en Chimie Organique, p. 249

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